Photo-induced oxidative synergistic degradation of mixed anionic/cationic surfactant systems in aqueous dispersions. A detailed study of the DBS/HTAB system

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ABSTRACT

The TiO_2-photoassisted degradations of the anionic dodecylbenzenesulfonate (DBS) and cationic hexadecyltrimethylammonium (HTAB) surfactants have been examined in aqueous media along with the cationic/anionic 1:1 binary complexes of DBS/HTAB. The processes were monitored by surface tension measurements, total organic carbon (TOC) assays and carbon dioxide evolution. The degradation of the anionic surfactant was significantly involved in prior adsorption of the species on the positively charged metal-oxide particle surface. By contrast, the degradation of the cationic surfactant was rather limited owing to the lack of adsorption on the TiO_2 surface under the same conditions. An adsorption model is proposed for the binary complexes on the metal-oxide surface.

1. Introduction

Surfactants are widely used in daily domestic applications such as household detergents, shampoos, rinses, and textile softeners. In household preparations, anionic surfactants such as sodium dodecylbenzenesulfonate (DBS), sodium dodecylsulfonate and the sodium salt of fatty acids are formulated with cationic surfactants such as benzyldimethyldodecyl-ammonium bromide, hexadecyltrimethylalkylammonium bromide and dodecylpyridinium chloride, and with the nonionic nonylphenylpolyethoxylate and alkylpolyethoxylate surfactants. The physico-chemical properties of mixed surfactant systems are well known to exhibit greater synergistic effects than those of single component systems [1]. These effects are due to complex formation and/or mixed micelle formation. Discharge of individual surfactants or mixed surfactant systems can lead to serious contamination of the aquatic ecosystems.

Cationic surfactants possess antibacterial and bactericidal disinfectant properties. Their bacterial degradability tends to be rather poor, so much as that it takes longer than a few months, if not years, to biodegrade cationic surfactants with bacteria. In this regard, biodegradation dynamics appear to depend on the chemical nature of the surfactants. Thus, a cationic surfactant exhibits poor biodegradability relative to an anionic surfactant: anionic surfactants > nonionic surfactants > cationic surfactants. Accordingly, a cationic surfactant tends to remain for some time in aquatic ecosystems without degrading thereby causing serious ecological damage to fish, water flea, algae and other aquatic living organisms; hence the need for novel treatment methods and sewage disposal facilities. By contrast, various treatments have been employed to degrade such systems to the extent that a cationic/anionic mixed surfactant system exhibits a synergistic effect with regard to surface-active properties and functionality. Nonetheless, details of the degradation remain somewhat elusive as is often evident in heterogeneous dispersions.

The photoassisted degradation of individual surfactants has been examined extensively in some earlier studies [2–8]. The photodegradability of surfactants in aqueous TiO_2 dispersions in terms of the chemical structure of the substrates has also been investigated [9].

Surfactant molecules are amphiphilic substances bearing water-soluble head groups and long hydrophobic alkyl chains. Accordingly, adsorption of a surfactant at a metal-oxide surface/water interface will play an important role in the degradation dynamics. An investigation of the adsorption behavior of surfactants on TiO_2 particles relevant to mixed micelle formation can provide useful information regarding potential (mechanistic) details of the photoassisted degradation. In this regard, it is useful to recall that the surface potential of TiO_2 is pH dependent such that the metal-oxide particle surface is positively charged in acidic media but negatively charged in alkaline media [8,9].

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In a recent article [10] we began a systematic examination of mixed surfactant systems. In the present article we examine further the influence of the co-existence of two different types of surfactants in the mixed systems involving the anionic dodecylbenzenesulfonate and the cationic hexadecyltrimethylammonium bromide surfactant, DBS/HTAB, in the overall photodegradation process at concentrations lower than their critical micelle concentrations (cmc). In particular, we examine the relationship(s) between the adsorption behavior of these binary systems on TiO_2 particles and their photoassisted decomposition in comparison with the relationships of their respective components. A possible adsorption model is described from an analysis of the degradation of the binary systems having different charged hydrophilic functions.

DBS
(cmc = 1.2 mM at 25 C)

HTAB
(cmc = 1.2 mM at 25 C)
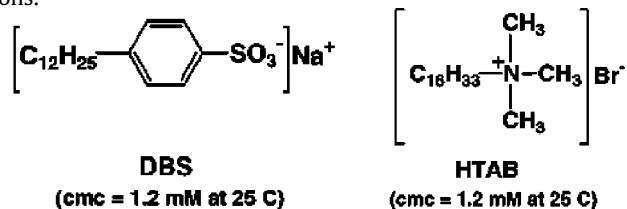
2. Experimental

2.1. Materials

The metal oxide TiO_2 was a kind gift from Degussa (P-25; 87% anatase and 13% rutile). The anionic surfactant sodium dodecylbenzenesulfonate {DBS; $[C_{12}H_{25}-C_6H_4-SO_3^-]$ Na^+} and the cationic surfactant hexadecyltrimethylammonium bromide (HTAB; $[C_{16}H_{33}-N^+(CH_3)_3]$ Br^-) were of reagent grade and were supplied by Tokyo Kasei Industries Co. Ltd. The critical micelle concentrations of DBS and HTAB are identical (cmc = 1.2 mM at 25 °C). The concentration ratios examined for the DBS/HTAB mixed solution are reported in Fig. 1. Two series of concentrations were prepared: (I) the total concentration of DBS and HTAB was kept constant at 0.10 mM while varying the ratio DBS and HTAB; and (II) the concentration of DBS was fixed at 0.10 mM and the concentration of HTAB was increased.

2.2. Photodegradation procedures

In each run, the total volume of each surfactant solution (*e.g.* 0.10 mM) was fixed at 50 mL. In binary surfactant systems, the total surfactant concentration was fixed at 0.10 mM. Thus, a 50-mL aqueous TiO_2 dispersion (TiO_2 loading, 2.0 g L^{-1}) of the surfactants was contained in a tightly closed 127-mL Pyrex cylindrical batch pho-
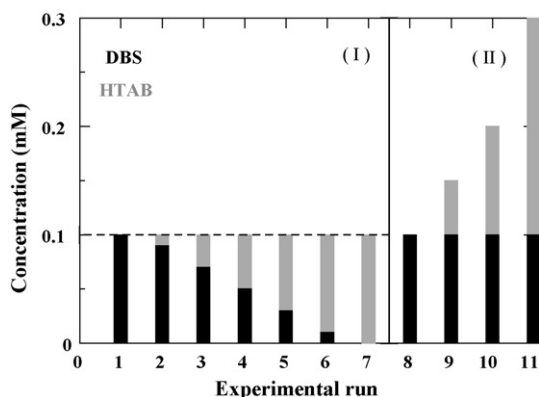

Fig. 1. Mixed molar ratios of anionic DBS and cationic HTAB surfactants examined (black = DBS; grey = HTAB); for meaning of (I) and (II) see text.

toreactor used to perform the photoassisted degradation reactions. The dispersion was initially sonicated for *ca.* 10 min. A magnetic stirrer guaranteed a satisfactory suspension and uniformity of the reacting mixture that had been pre-saturated with O_2 gas by purging with pure oxygen at atmospheric pressure for *ca.* 20 min prior to irradiation. The photoreactor was irradiated externally with a 75-Watt super high-pressure Hg lamp (Toshiba SHL-100UVQ2). During the photodegradation, the photoreactor was air-cooled with a fan; the suspension temperature was *ca.* 313 K (~40 °C). The light irradiance impinging on the suspension was *ca.* 2 mW cm^{-2} (wavelength range, 310–400 nm; maximal emission, 360 nm) as measured with a Topcon UVR-2 radiometer. All analyses were performed after removal of the TiO_2 particles by centrifugation and eventual filtration with an Advantec 0.20 (m PTFE filter.

The total organic carbon (TOC) remaining in the suspensions for each degraded solution of surfactant(s) after a finite UV illumination time was analyzed with a Shimadzu TOC-5000A total organic carbon analyzer. The surface tensions were measured as a function of UV illumination time at ambient temperature with a CBVP-Z automatic surface tensiometer (Kyowa Interface Science Co. Ltd.). The disappearance of the aromatic ring absorption in the surfactant structures was monitored with a JASCO V-570 UV spectrophotometer, whereas the evolution of CO_2 during the photoreaction was assayed as a function of time using a Shimadzu GC-8AIT gas chromatograph equipped with a Shimadzu Porapack Q 80–100 column (for CO_2 evolution) linked to a TCD detector; helium was the carrier gas. Formation of NH_4^+, NO_3^- and SO_4^{2-} ions was assayed by high-pressure liquid chromatography {Jasco; CD-5 conductivity detector; Shodex cationic (Y-521) and anionic (I-524) columns}. The eluent was a 4 mM HNO_3 solution for the cationic column or a solution of phthalic acid (2.5 mM) and tris(hydroxymethyl)aminomethane (2.3 mM) for the anionic column. Analyses were performed after separation of the metal oxide by centrifugation and eventual filtration on an Advantec 0.20 μm PTFE filter. In alkaline media, the NH_3 produced (if any) was detected as NH_4^+ ions on acidification with the HNO_3 eluent during the analyses for cations.

3. Results and discussion

3.1. Surface tension and photodegradation of DBS/HTAB mixed surfactants

The concentration dependence of the surface tension in mixed aqueous surfactant systems of DBS/HTAB reported in Fig. 2a shows that both HTAB and DBS surfactants exhibit a sharp breakpoint at 1.2 mM, whereas the DBS/HTAB binary system shows that the cmc decreased nearly 6-fold to *ca.* 0.02–0.03 mM [10]. According to the Gibbs adsorption isotherm equation, the linear steep slope below the cmc indicates that the amount of surfactant adsorbed in the mixed system was greater than the quantity adsorbed for each surfactant system. It further suggests that the mixed surfactant molecules at the air/water interface are closely packed or otherwise closely oriented.

The surface tension behavior during the photoassisted degradation of aqueous HTAB and DBS metal-oxide dispersions, and the TiO_2 dispersion of the DBS/HTAB binary system are illustrated in Fig. 2b. All experiments were carried out at a fixed concentration of surfactants (0.10 mM, 50 mL) in the presence of TiO_2 particles (loading, 100 mg; 2 g L^{-1}) under oxygenated conditions.

The degradation process monitored by the time profiles of the surface tension shows an initial surface tension of the DBS/HTAB aqueous solution (no TiO_2) of 30 mN m^{-1}. In the presence of TiO_2, however, the surface tension of the mixed solution increased to about 60 mN m^{-1}. This abrupt rise of the surface tension is caused
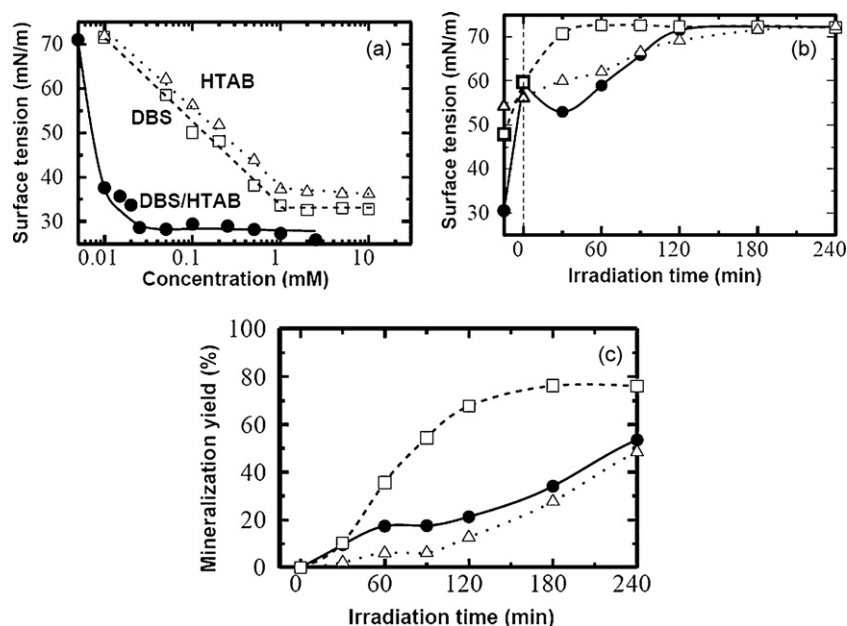
Fig. 2. (a) Concentration dependence of the surface tension of individual surfactant solutions and solutions of the mixed DBS/HTAB (molar ratio 1:1) binary system at ambient temperature. (b) Surface tension behaviors against irradiation time for the binary systems (●; total volume, 50 mL; DBS, 0.20 mM, 25 mL; HTAB, 0.20 mM, 25 mL); for the DBS solution alone (□; 0.10 mM, 50 mL), and for the HTAB solution alone (△; 0.10 mM, 50 mL); TiO$_2$ loading was 100 mg in 50 mL solution. (c) Mineralization yield of the mixed binary HTAD/DBS system against irradiation time in comparison with that of HTAB and DBS solutions alone: DBS/HTAB (●); HTAB (△); and DBS (□). Total volume of the mixed binary solution, 50 mL, containing DBS (0.20 mM, 25 mL) and HTAB (0.20 mM, 25 mL); solutions of DBS alone, 0.10 mM, 50 mL; and HTAB alone, 0.10 mM, 50 mL; TiO$_2$ loading, 100 mg in 50 mL dispersions. From Ref. [10]; Copyright 2008 by Science and Technology Network, Inc.

by the adsorption of the mixed surfactant onto the TiO$_2$ surface. In the initial stages of irradiation, the surface tension temporarily decreased (some of the binary complex desorbed during this period) and then gradually increased with further irradiation to attain the surface tension of water (72 mN m^{-1}). By contrast, the surface tensions for the individual HTAB and the DBS surfactants increased gradually against irradiation time. Based on the increase of surface tension alone, we infer that the cationic HTAB surfactant degraded slower than DBS.

The mineralization yield evaluated by CO$_2$ generation was about 78% for DBS and 67% for HTAB after a 240-min UV irradiation time (Fig. 2c). Generation of CO$_2$ gas for DBS was faster than for HTAB, and concomitantly the mineralization dynamics of the binary mixed system are also faster than the rate of mineralization of HTAB, albeit remarkably slower than for DBS alone. Evidently, the HTAB surfactant in the binary system drags down the degradation of the DBS. Since TiO$_2$ is positively charged in acidic media, the anionic DBS surfactant is adsorbed on the metal-oxide surface and reacts as a surface DBS adsorbate with photogenerated •OH radicals produced through the oxidation of surface H$_2$O or OH$^-$ ions. In fact, the photodegradation of DBS was such that we failed to detect hydroxylation of the benzene ring in DBS by the time-of-flight mass spectrometric technique [10], suggesting rapid cleavage of the aromatic ring followed by fairly rapid formation of carboxyl and/or carbonyl intermediates, ultimately leading to the generation of CO$_2$ gas. By contrast, the remarkably slow decomposition of HTAB must be due, at least partially, to repulsion between the cationic charge of HTAB and the positively charged TiO$_2$ surface. The surface charge of TiO$_2$ particles is considerably weakened in the mixed binary system.

The temporal behavior of TOC loss illustrated in Fig. 3 confirms the inference that the DBS/HTAB binary system adsorbed almost completely (ca. 90%) on the TiO$_2$ particle surface in the initial (dark) stage. Note that the binary complexes are water-insoluble at high concentrations, but at concentrations near or below the cmc (see above), the 1:1 complex is water-soluble. Upon irradiation the TOC

increased attaining a maximum after ca. 75 min indicating a gradual photodesorption of the adsorbed complex during the initial stages of UV irradiation, after which the level of TOC in the dispersions decreased with the evolution of carbon dioxide. By comparison, adsorption of the cationic HTAB on the positively charged TiO$_2$ surface was negligibly small owing to Coulombic repulsion. Upon UV irradiation, a gradual decrease of TOC was observed, followed by a rather slow decomposition up to 240 min. The extent of initial adsorption of the anionic DBS surfactant on the TiO$_2$ particle surface was considerable relative to HTAB (ca. 50%). In the first 30 min of UV irradiation, the DBS surfactant also somewhat photodesorbed followed by a relatively fast decrease of TOC relative to HTAB.

As a further confirmation of degradation of DBS alone or in the DBS/HTAB binary systems at different ratios, we monitored the time course of benzene ring cleavage by the benzene ring spectral band positioned at 224 nm; results are displayed in Fig. 4. The extent of adsorption of this anionic surfactant (0.10 mM) onto
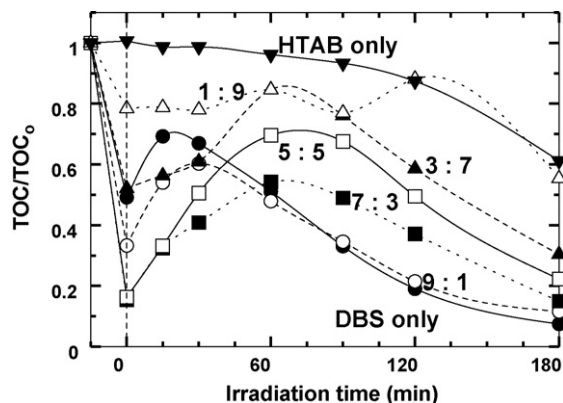

Fig. 3. Temporal course of the photoassisted mineralization monitored as the TOC loss at different ratios of the mixed DBS/HTAB surfactant solutions.
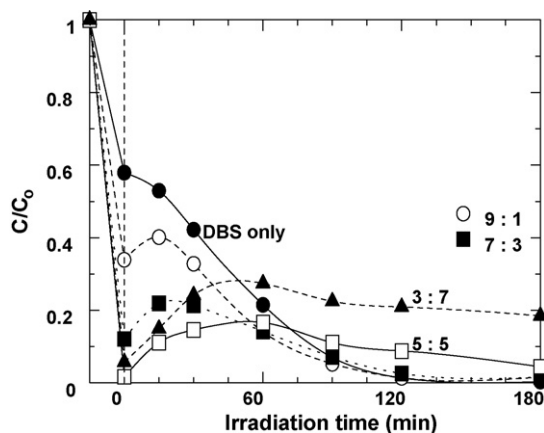
Fig. 4. Aromatic ring disappearance of DBS for DBS/HTAB ratio against irradiation time. Experimental conditions are similar to those mentioned in Fig. 2b.

Fig. 6. Effect of the addition of HTAB on the disappearance of the aromatic spectral peak of DBS (concentration maintained constant at 0.10 mM); vertical dashed line: 1:1 ratio of DBS/HTAB (0.10 mM/0.10 mM).

the TiO_2 surface prior to irradiation was *ca.* 40%. Near complete transformation of the aromatic ring of DBS occurred rather rapidly within 120 min of UV illumination. At the larger ratios of DBS (9:1 and 7:3) in suspensions of DBS/HTAB mixed surfactants, ring opening in the DBS structure was again relatively fast. At a ratio of 5:5 for DBS/HTAB, the absorption was the least intense that is taken as evidence of formation of the 1:1 complex between the two surfactants. In any case, whenever the concentration of the cationic surfactant HTAB was equivalent to or larger than that of DBS, degradation of DBS tended to be relatively slow.

The extent of formation of ionic species from the TiO_2-photoassisted mineralization of the DBS/HTAB suspensions at different ratios of DBS and HTAB, together with ring cleavage and extent of TOC loss after nearly 180 min of UV illumination are illustrated in Fig. 5. The yield of ring opening of the aromatic group increased with increasing DBS/HTAB ratio attaining 100% for a DBS concentration of 0.10 mM (no HTAB present). Whenever the HTAB concentration was greater than that of DBS, cleavage of the benzene ring in DBS was somewhat depressed. The extent of mineralization of the DBS/HTAB suspensions, as attested by the extent of TOC loss, also increased with the greater quantities of DBS present in the mixed suspensions. Formation of SO_4^{2-} ions followed a similar trend reaching *ca.* 50% in the bulk solution with the remainder being adsorbed onto the TiO_2 surface.

Transformation of the nitrogen function in HTAB gave only a slight amount of NH_4^+ ions. However, in the mixed DBS/HTAB suspensions no NH_4^+ ions were detected and likely none formed in any detectable quantity. The amount of NO_3^- ions formed was highest when the DBS/HTAB ratio was 1:9 and tended to decrease with an increase in the amount of DBS.

The data reported in Fig. 6 also confirm the formation of the 1:1 complex between DBS and HTAB in displaying the lowest absorbance at 224 nm for the benzene ring of DBS at the longer irradiation times. Under dark conditions ($t = 0$ min), mixed micelles formed in the initial DBS/HTAB solution (0.10 mM/0.10 mM). The composition ratio of the micelles is estimated to exhibit a cationic surfactant-rich micelle aggregate. After 15–30 min of UV illumination, the intensity of the 224-nm absorption band of the benzene ring of DBS increased, and since the relative ratio of DBS was higher, the absorption increase may be due to the formation of some hydroxylated aromatic intermediate(s) under these conditions. However, after 60 min of illumination the benzene ring spectral feature gradually disappeared. The cationic HTAB surfactant, which bears no aromatic ring, impacts on the ring opening of DBS. No mixed micelles were evident after more than 90 min of illumination.

3.2. Proposed adsorption model

Surfactants present at low concentrations in bulk solution generally exist in monomer-like form. However, at concentrations greater than the cmc of the respective surfactants, formation of mixed micellar aggregates can occur as illustrated in the cartoon of Scheme 1. This is a characteristic feature of surfactants in that a monomer in solution tends to form aggregates or micelles above
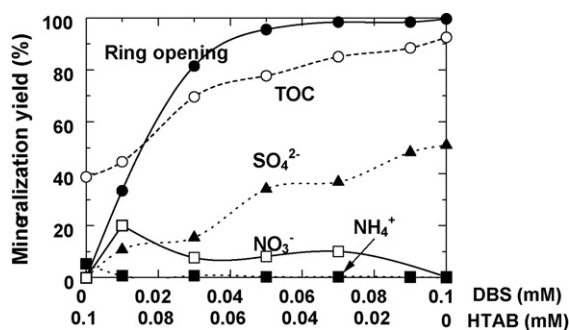

Fig. 5. Dependence of the molar DBS/HTAB ratio on the mineralization process in the aqueous mixed surfactants after a long illumination time (180 min). Experimental conditions are similar to those mentioned in Fig. 2b.
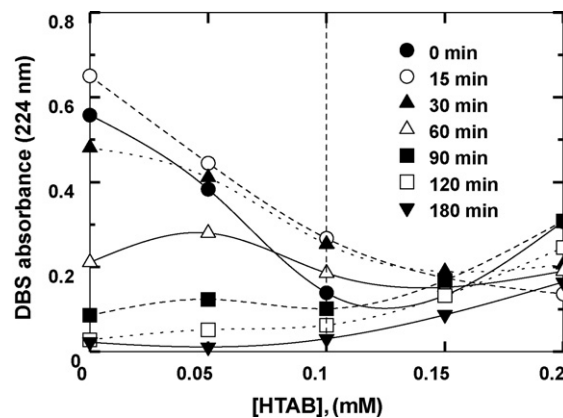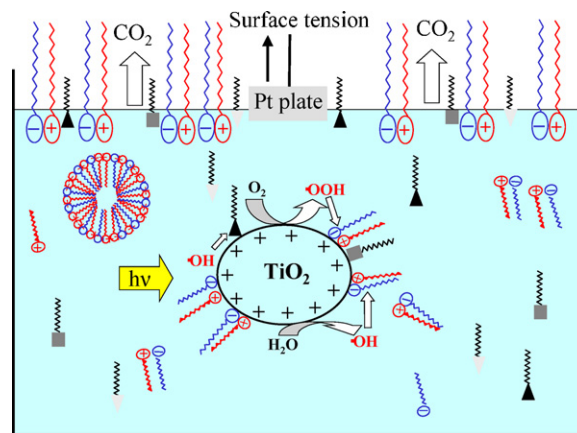

Scheme 1. Schematic model of the photo-induced oxidation mechanism for the binary cationic/anionic surfactant complexes at the air/water interface. Various types of shorter carboxylate and/or aldehyde intermediates may be generated in the aqueous bulk solution.

the cmc. The cmc for the DBS/HTAB system decreases relative to the cmc's of HTAB and DBS (Fig. 2). In the mixed DBS/HTAB aqueous system, ion-pairs formed between DBS and HTAB co-exist as monomer species with the mixed micelles. Such ion-pairs have a tendency to be adsorbed at the air/water interface as well as at the TiO_2/surfactant solution interfaces as depicted in Scheme 1.

Most of the initial cationic surfactants are adsorbed on the positively charged TiO_2 surface through the synergistic effect of the anionic surfactants in the binary complexes to form the hemi-micellar aggregates. Undecomposed cationic surfactants located at the air/water interface cause the surface tension to be relatively low. However, with the increase of UV irradiation time, various intermediates from the cationic surfactants are generated and are oriented at the air/water interface. Accordingly, the concentration of the intermediates at the interface increases leading to a higher surface tension. As the mineralization of various intermediates that were produced in the process occurred, the surface tension tended toward the surface tension of water.

Failure of the cationic HTAB surfactant to be adsorbed on the TiO_2 surface in bulk solution causes the cationic and anionic surfactant to form a 1:1 complex, which is then followed by adsorption onto the TiO_2 surface as a "Gemini"-type system bearing two long alkyl chains (Scheme 1). Subsequent to the photogeneration of $^\bullet$OH radicals, these radicals attack the anionic entity of the 1:1 complex at the benzene ring of DBS. Immediate oxidation takes place to generate water-soluble intermediates, such as short-chain aldehydes and/or carboxylic acids. In some cases the hydrophilic and lipophilic balance of an amphiphilic substance turns around so that the hydrophobic intermediates are oriented at the air/water interface. Such oxidation processes continue ultimately leading to the evolution of carbon dioxide.

4. Concluding remarks

A 1:1 complex is formed in bulk aqueous solution between the anionic DBS surfactant and the cationic HTAB analog, a complex that behaves as a Gemini-type surfactant bearing two long alkyl chains, followed by adsorption of the head groups on the positively charged TiO_2 surface. This position is suitable for the photogenerated $^\bullet$OH radicals to attack the electron-rich aromatic ring of DBS to produce various intermediates (not identified in the present study, but likely aldehydes and/or carboxylic acids) that fairly rapidly also undergo disintegration and degradation to the ultimate product carbon dioxide. By contrast, the cationic HTAB desorbs from the TiO_2 surface into the bulk aqueous solution and subsequently undergoes a rather slow degradation.

It is typical of $^\bullet$OH radicals to attack an electrophilic function in a surfactant molecule. For instance, the benzene function that possesses a high density of (electrons is rapidly degraded with respect to the slower degradable alkyl chains. The $^\bullet$OH radicals and H^+ species are equally formed during the photoassisted oxidation of H_2O, with the latter species chemisorbing on the TiO_2 surface, and in turn imparting a positive charge to the metal-oxide particles. This leads to an enhanced adsorption of anionic surfactants on the TiO_2 surface, which in turn causes an acceleration of the degradation of the surfactants. By contrast, electrostatic repulsion between the cationic surfactant molecules and the positively charged metal-oxide surface makes it difficult for such molecules to approach the TiO_2 surface, thereby slowing down the degradation of such substrates. The present results also re-affirm the notion that attachment of surfactant molecules – or any substrate for that matter – onto the TiO_2 particle surface plays an important role in the overall mineralization of environmental contaminants.

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